PART 4

LM2-TOXIC

Chapter 3. Model Description

As one of the submodels in the overall Lake Michigan Mass Balance Project (LMMBP) modeling framework, LM2-Toxic was specifically developed to simulate transport and fate of toxic chemicals, such as polychlorinated biphenyl (PCB) congeners, in both the water and sediment of Lake Michigan. The principal focus of this model was to quantitatively define the relationship among external carbon and toxic chemical loads, internal cycling of organic carbon and toxic chemicals, and toxic chemical concentrations in the water and sediments of the lake. The PCB exposure concentrations predicted from the LM2-Toxic model were then used as a forcing function to compute PCB concentrations in fish tissue.

LM2-Toxic evolved by combining the IPX and GBTOX models in an attempt to better represent and integrate processes considered to be important in Lake Michigan (Velleux *et al.*, 2000; Settles, 1997; Bierman *et al.*, 1992). Both the IPX and GBTOX are descendants from the WASP4 water quality modeling framework (Ambrose *et al.*, 1988).   LM2-Toxic incorporates the organic carbon dynamics highlighted in GBTOX and the sediment transport scheme, a quasi-Lagrangian framework, used in the IPX model. It allows decay and transformation between organic carbon states in both the water column and sediment bed and variation of the surficial sediment layer thickness in response to net settling or net resuspension of sediments. In addition to the above features, an updated air-water exchange formulation (Bamford *et al.*, 1999; Wanninkhof *et al.*, 1991;

Schwarzenbach *et al.*, 1993) was implemented in the model.

4.3.1 Model Framework

LM2-Toxic was based on the principle of conservation of mass. It used the same finite segment modeling approach used in the United States Environmental Protection Agency (USEPA)-supported WASP4 modeling framework. The mass of a chemical or solid in each segment of a water system is controlled by water movement between adjacent segments, solid dynamics and chemical dynamics within the system, internal and external loads, and boundary concentrations. A group of mass balance equations representing the above processes was used in the model to compute change of mass for a state variable (constituent) in a segment at a certain time. The model traced and described where and how a mass of constituent was transported and transformed. The general time-dependent finite differential equation in a given segment can be written to describe the change of mass for a state variable at a certain time.

In a water column segment:

$$V_j \frac{dC_j}{dt} = \sum_i^n Q_{ij} C_{ij} + \sum_i^n R_{ij}(C_i - C_j) + W_j + S_{aw,j} + S_{sw,j} + S_{k,j}$$

(4.3.1.)

In a sediment segment (assume mixing only in vertical direction):

$$V_j \frac{dC_j}{dt} = \sum_i^n R_{ij}(C_i - C_j) + S_{sw,j} + S_{b,j} + S_{k,j} \quad (4.3.2)$$

where

V_j =   volume of segment j (L^3)

C_j =   concentration of water quality constituent in segment j (M/L^3)

C_{ij} =   concentration of water quality constituent at the interface between segment i and j (M/L^3)

Q_{ij} =   net flow across the interface between segment i and j (defined as positive when entering segment j and negative when leaving segment j) (L^3/T)

n =   number of adjacent segments

R_{ij} =   ($E_{ij}A_{ij}/\Delta X_{ij}$), bulk dispersion/diffusion coefficient (L^3/T)

E_{ij} =   mixing (dispersion/diffusion) coefficient (L^2/T)

A_{ij} =   interfacial area between segment i and j (L^2)

ΔX_{ij} =   characteristic mixing length between segments i and j (L)

W_j =   internal and external loading rate of segment j (M/T)

$S_{aw,j}$ =   mass change rate due to air-water exchange process between segment j and air directly above segment j (M/T)

$S_{sw,j}$ =   mass change rate due to sediment-water exchange processes between segment j and adjacent sediment segments (M/T). The processes include settling and resuspension

S_k =   mass change rate due to sum of kinetic transformation processes within segment j (M/T), positive is source, negative is sink

S_b =   mass change rate due to burial process from surficial mixing layer to deeper sediment layer (M/T)

Note: L = length; M = mass; T = time.

The following sections of this chapter will provide a detailed description of model segmentation, water circulation, solid dynamics, and chemical dynamics. The direct loads, including external and internal loads, and boundary conditions are discussed in detail in Chapter 4.

4.3.2 Model Configuration

4.3.2.1 Spatial Resolution – Segmentation

Compared to MICHTOX (Level 1 contaminant transport and fate model developed for Lake Michigan) segmentation (Figure 3.3.2), the LM2-Toxic Level 2 model had finer resolution. Most water column segments in the LM2-Toxic model segmentation share the same or portion of the segment boundaries used in the MICHTOX-Toxic model. Green Bay segments had similar features as those used in GBTOX (Bierman *et al*., 1992) and MICHTOX (Endicott *et al*., 2005). The significant differences between Level 1 and Level 2 models were with respect to model structure, state variables, and related physical and chemical processes. They are discussed in detail in the following sections.

The spatial segmentation for the LM2-Toxic model was developed from digitized bathymetric (5 x 5 km^2 grid) and shoreline data for Lake Michigan provided by Dr. David Schwab, National Oceanic and Atmospheric Administration (NOAA) (Schwab and Beletsky, 1998). The lake, including Green Bay, was divided into 10 horizontal columns, five water column layers, and one surficial sediment layer. A detailed spatial and cross sectional segmentation of the LM2-Toxic model is illustrated in Figures 4.3.1 to 4.3.3. There are 94 segments in total. Segments 1-41 were water column segments. Most of them had an interface with surficial sediments. Segments 1-10 were surface water segments with an interface with the atmosphere. Segments 42-94 were the surficial sediment segments with sizes not identical to the upper water column segments. The sediment segmentation of the LM2-Toxic model was very
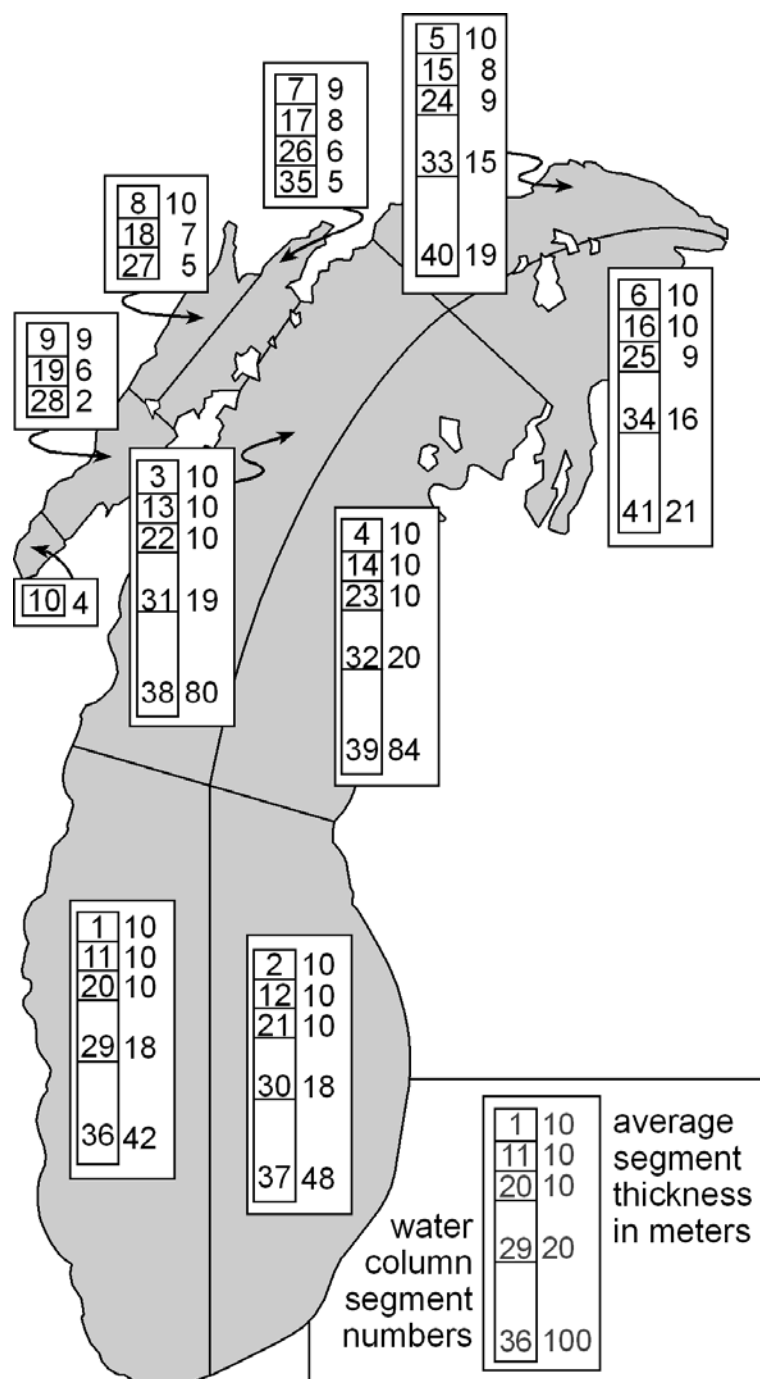
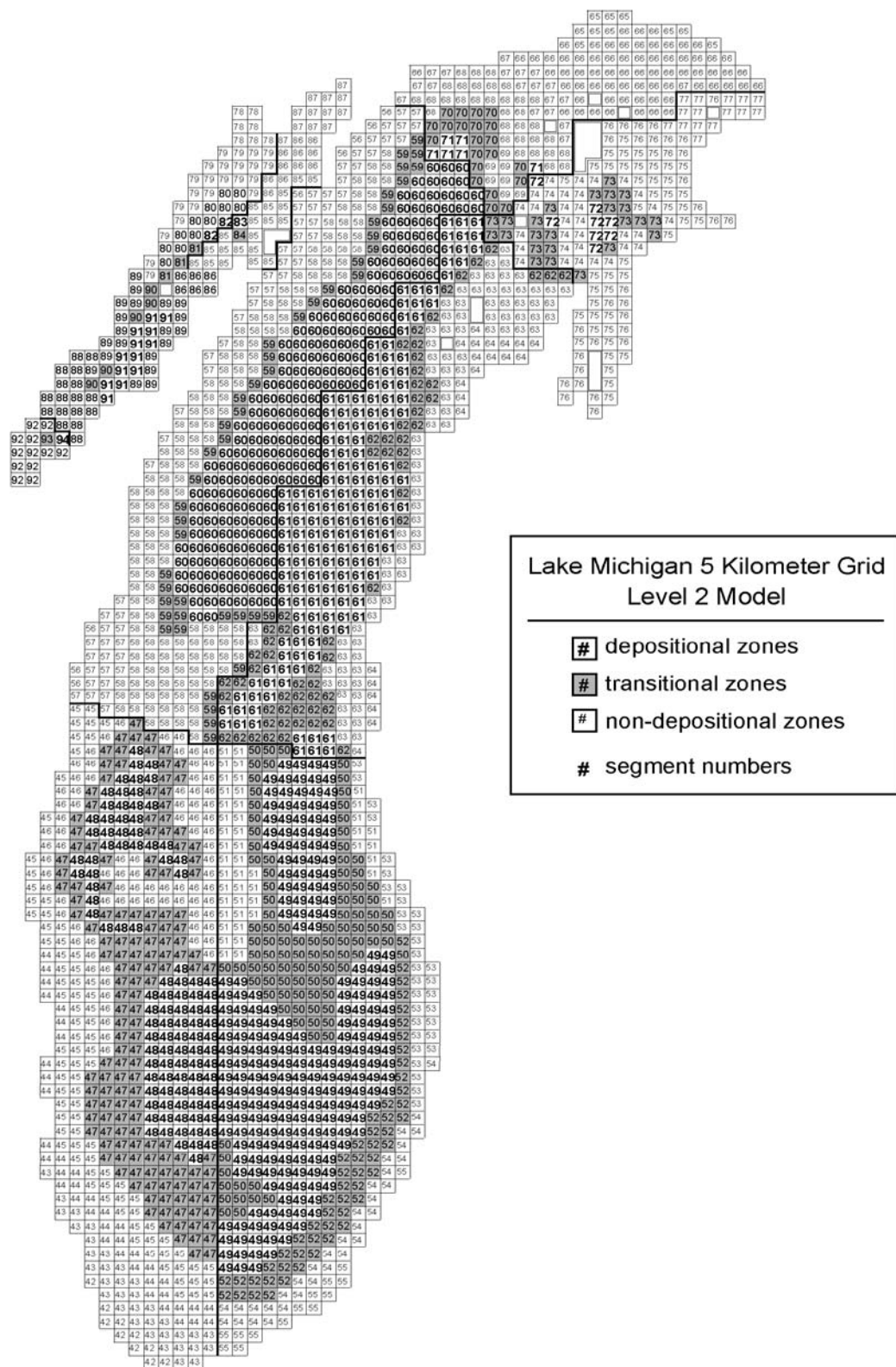**Figure 4.3.1. Water column segmentation for the LM2-Toxic model.**

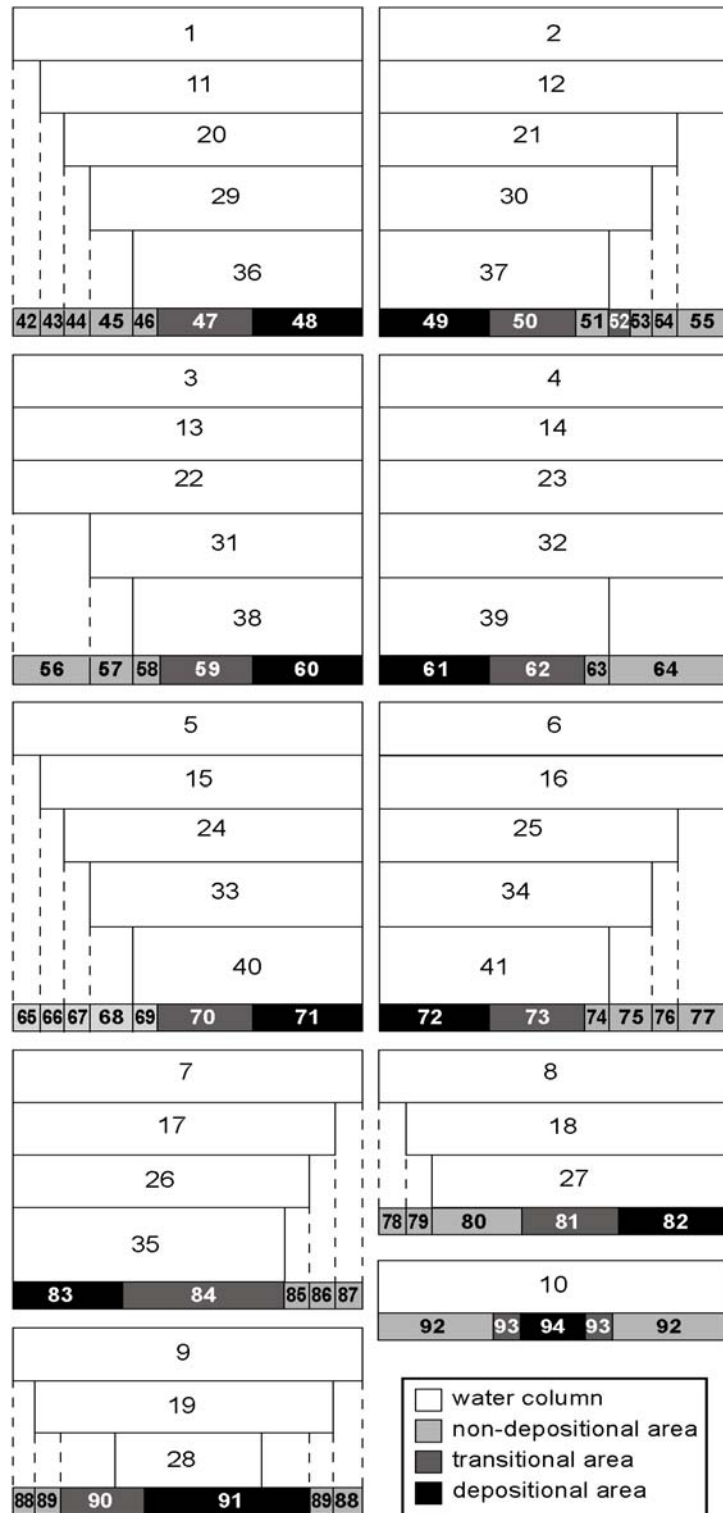**Figure 4.3.2. Surface sediment segmentation for the LM2-Toxic model.**

Figure 4.3.3. Cross-sectional sediment segmentation and overlying water column segments for 10 Lake Michigan and four Green Bay water columns.

227

different from the one used in MICHTOX. The surficial sediment was differentiated into non-depositional areas, transitional areas, and depositional areas (Figure 4.3.2). The areas in a surficial sediment segment were not necessarily adjacent to each other. The surficial mixing sediment layer was not uniformly distributed and its thickness varied from 1 to 4 cm in transitional and depositional areas.

The principal criteria considered for the LM2-Toxic model water column segmentation were the following:

1. Circulation patterns (Schwab and Beletsky, 1998).

2. Bathymetry (Schwab and Beletsky, 1998).

3. Horizontal and vertical gradients of temperature and concerned constituent concentrations.

4. Comparability to MICHTOX segmentation and its results.

The principal criteria considered for the LM2-Toxic model surficial sediment segmentation were the following:

1. Bathymetry data – 5 x 5 km grid (Schwab and Beletsky, 1998).

2. Distribution of sediment characteristics (Cahill, 1981; Robbins *et al.*, 1999).

3. Results generated from the LMMBP sediment measurements – box cores, ponar, and gravity samples (Robbins *et al.*, 1999; Eadie and Lozano, 1999).

Geometry-related data used in the LM2-Toxic model such as volumes, surface areas, and average thickness of all segments are listed in Tables 4.3.1 and 4.3.2.

4.3.2.2 Temporal Resolution

Two levels of temporal resolution for model inputs and outputs were applied to LM2-Toxic. One was a daily time scale that was used for the LM2-Toxic calibrations. Another was a monthly time scale that

was used for the purpose of long-term forecasts to be used as a lake management tool. Both temporal resolutions were detailed enough for physical and chemical processes in the lake that occur at monthly or seasonal time scales, such as thermal stratification, general water circulation patterns, carbon internal loads (primary production), PCB atmospheric concentrations, and resuspension. Final interpretation of carbon and PCB mass budgets and the results from long-term load reduction scenarios on a lake-wide basis were at an annual time scale using annually averaged results.

4.3.3 Water Balance

Water balance is one of the major components in a traditional water quality modeling framework. Water movement directly controls the transport of solids and chemicals in dissolved and particulate phases in a water system. In terms of LM2-Toxic model inputs, the data in transport fields such as advective flows and dispersive exchanges or mixing were used to describe the water balance in the model. The components and their sources used in LM2-Toxic model transport fields are listed below:

1. Bi-direction horizontal advective flows (provided by David Schwab, NOAA; originally based on Schwab and Beletsky, 1998).

2. Net vertical advective flows (provided by David Schwab, NOAA; originally based on Schwab and Beletsky, 1998).

3. Tributary flows and flows across the Straits of Mackinaw (Endicott *et al.*, 2005; Quinn, 1977).

4. Water balancing flows.

5. Vertical dispersion coefficients.

Components such as precipitation, evaporation, and groundwater infiltration were not considered in the water transport fields used in the LM2-Toxic model.

Correct water circulation is essential for the accuracy of outputs from the LM2-Toxic model. The Princeton Ocean Model (POM) has been demonstrated for its ability to accurately simulate water movement for a given large water body (Schwab and Beletsky, 1997; Blumberg and Mellor, 1987). Using an extensively

Table 4.3.1. Geometry Data for Water Column Segments and Lake Michigan (Total)

Segment Number	Volume (m^3)	Average Thickness (m)	Surface Area (m^2)	Water Segment Above
1	1.2729E+11	9.97	1.2750E+10	
2	1.3000E+11	10	1.3000E+10	
3	1.1475E+11	10	1.1475E+10	
4	8.6000E+10	10	8.6000E+09	
5	4.0850E+10	9.95	4.1000E+09	
6	3.8500E+10	10	3.8500E+09	
7	1.1925E+10	9.25	1.2750E+09	
8	1.1475E+10	9.7	1.1750E+09	
9	1.3213E+10	9.49	1.3750E+09	
10	1.7250E+09	4.36	3.5000E+08	
11	1.2123E+11	9.66	1.2500E+10	1
12	1.2924E+11	9.93	1.3000E+10	2
13	1.1475E+11	10	1.1475E+10	3
14	8.6000E+10	10	8.6000E+09	4
15	3.1775E+10	8.05	3.8500E+09	5
16	3.7263E+10	9.63	3.8500E+09	6
17	8.4125E+09	8.44	9.7500E+08	7
18	7.7625E+09	7.48	1.0000E+09	8
19	6.4375E+09	6.34	9.5000E+08	9
20	1.1214E+11	9.6	1.1625E+10	11
21	1.2303E+11	9.69	1.2650E+10	12
22	1.1444E+11	9.97	1.1475E+10	13
23	8.6000E+10	10	8.6000E+09	14
24	1.9625E+10	8.99	2.1500E+09	15
25	3.1988E+10	9.1	3.4750E+09	16
26	3.7625E+09	6.36	5.5000E+08	17
27	2.1500E+09	4.53	4.2500E+08	18
28	5.3750E+08	2.13	2.0000E+08	19
29	1.9198E+11	18.01	1.0600E+10	20
30	2.1649E+11	18.22	1.1825E+10	21
31	2.1339E+11	18.85	1.1275E+10	22
32	1.6908E+11	19.63	8.6000E+09	23
33	2.4813E+10	14.55	1.6750E+09	24
34	4.2725E+10	15.63	2.7000E+09	25
35	2.8750E+08	4.5	5.0000E+07	26
36	3.6038E+11	42.01	8.4750E+09	29
37	4.6783E+11	48.1	9.6250E+09	30
38	7.8266E+11	79.58	9.8000E+09	31
39	6.8133E+11	84.05	8.0750E+09	32
40	1.6913E+10	19.38	8.5000E+08	33
41	3.4625E+10	21.11	1.6000E+09	34
Total	4.8148E+12		5.7950E+10	

Table 4.3.2. Initial Geometry Data for Surficial Sediment Segments and Surficial Sediment Layer (Total)

Segment Number	Volume (m³)	Average Thickness (m)	Surface Area (m²)	Water Segment Above
42	2.5000E+05	0.001	2.5000E+08	1
43	8.7500E+05	0.001	8.7500E+08	11
44	1.0250E+06	0.001	1.0250E+09	20
45	2.1250E+06	0.001	2.1250E+09	29
46	2.6975E+07	0.013	2.0750E+09	36
47	6.8850E+07	0.018	3.8250E+09	36
48	6.4375E+07	0.025	2.5750E+09	36
49	1.8058E+08	0.031	5.8250E+09	37
50	7.6850E+07	0.029	2.6500E+09	37
51	2.1850E+07	0.019	1.1500E+09	37
52	1.6500E+07	0.012	1.3750E+09	30
53	8.2500E+05	0.001	8.2500E+08	30
54	8.2500E+05	0.001	8.2500E+08	21
55	3.5000E+05	0.001	3.5000E+08	12
56	2.0000E+05	0.001	2.0000E+08	22
57	1.4750E+06	0.001	1.4750E+09	31
58	4.9725E+07	0.013	3.8250E+09	38
59	2.1850E+07	0.019	1.1500E+09	38
60	1.3510E+08	0.028	4.8250E+09	38
61	1.0985E+08	0.026	4.2250E+09	39
62	5.0375E+07	0.031	1.6250E+09	39
63	3.5600E+07	0.016	2.2250E+09	39
64	5.2500E+06	0.010	5.2500E+08	32
65	2.5000E+05	0.001	2.5000E+08	5
66	1.7000E+06	0.001	1.7000E+09	15
67	4.7500E+05	0.001	4.7500E+08	24
68	8.2500E+05	0.001	8.2500E+08	33
69	1.7500E+06	0.010	1.7500E+08	40
70	1.2600E+07	0.024	5.2500E+08	40
71	4.5000E+06	0.030	1.5000E+08	40
72	2.0000E+06	0.010	2.0000E+08	41
73	6.8750E+06	0.011	6.2500E+08	41
74	7.7500E+06	0.010	7.7500E+08	41
75	1.1000E+06	0.001	1.1000E+09	34
76	7.7500E+05	0.001	7.7500E+08	25
77	3.7500E+05	0.001	3.7500E+08	16
78	7.0000E+06	0.04	1.7500E+08	8
79	2.3000E+07	0.04	5.7500E+08	18
80	1.2000E+07	0.04	3.0000E+08	27
81	3.0000E+06	0.04	7.5000E+07	27
82	2.0000E+06	0.04	5.0000E+07	27
83	1.0000E+06	0.04	2.5000E+07	35
84	1.0000E+06	0.04	2.5000E+07	35
85	2.0000E+07	0.04	5.0000E+08	26
86	1.7000E+07	0.04	4.2500E+08	17
87	1.2000E+07	0.04	3.0000E+08	7
88	1.7000E+07	0.04	4.2500E+08	9
89	2.0000E+07	0.04	5.0000E+08	19
90	5.0000E+06	0.04	1.2500E+08	19,28
91	1.3000E+07	0.04	3.2500E+08	19,28
92	1.2000E+07	0.04	3.0000E+08	10
93	1.0000E+06	0.04	2.5000E+07	10
94	1.0000E+06	0.04	2.5000E+07	10
Total	1.0871E+09		5.7950E+10	

tested version of POM for the Great Lakes (POMGL), transport fields were generated for Lake Michigan at different spatial and temporal resolutions for use in a series of mass balance models adapted for LMMBP (Schwab and Beletsky, 1998). The hydrodynamic model for Lake Michigan had 20 vertical levels and a uniform horizontal grid size of 5 km (Schwab and Beletsky, 1998). Because the LM2-Toxic model segmentation was constructed based on the 5 x 5 km^2 grid used in the POMGL for Lake Michigan, the hydrodynamic model results were easily aggregated to the resolution used in LM2-Toxic (Schwab and Beletsky, 1998). The aggregated horizontal bi-direction flows at each interface provided a good approximation of horizontal advective and dispersive transport components at the interface. The advantage of using bi-direction flows at an interface was that it bypassed the tedious and necessary horizontal dispersion coefficient calibration procedure required when only net flow is available at the interface.

The vertical transport field was calculated in the form of net vertical flow (provided by David Schwab, NOAA; originally based on Schwab and Beletsky, 1998). Therefore, vertical exchange coefficients were calculated and calibrated to define the vertical mixing process between vertically adjacent segments. A summer period of strong stratification and a non-stratified period of intense vertical mixing were the most important limnological features of the Great Lakes (Chapra and Reckhow, 1983; Thomann and Mueller, 1987). Therefore, determining the dynamics of vertical mixing was considered as an important task in modeling development for the LMMBP. A thermal balance model was constructed to calibrate the vertical exchange coefficients at the interfaces (Zhang *et al.*, 1998, 2000). The coefficients were calibrated using 250 observed vertical temperature profiles collected at 40 stations in Lake Michigan during the 1994-1995 LMMBP period. The model calibration results versus temperature measurements in each water column segment and temporal plots of calibrated exchange coefficients are listed in Appendix 4.5.1. A detailed discussion on how the thermal model was run can be found in Part 4, Chapter 4.

Water balancing flow was another advective component added into the water transport field for LM2-Toxic. The aggregated advective flows provided by NOAA were not balanced in individual segments over the two-year LMMBP period. However, the total water mass was perfectly balanced on a whole lake basis. Over the two-year LMMBP period, some segments lost or gained a certain amount of water. This problem could be very significant for long-term simulations for the LM2-Toxic. It stops the model simulation once the volume of a segment reached zero. To counter the amount lost or gained in each segment, a balancing flow was introduced to keep the volume of water unchanged in each segment at any time during the simulation. The balancing flows were generated based on the aggregated advective flows (provided by David Schwab, NOAA; originally based on Schwab and Beletsky, 1998), original volume of each segment, and the general water circulation patterns during the LMMBP period.

Tributary flows and flows through the Straits of Mackinac were based on MICHTOX model inputs (Endicott *et al.*, 2005), literature (Quinn, 1977), and water circulation patterns during the LMMBP period (provided by David Schwab, NOAA; originally based on Schwab and Beletsky, 1998).

After vertical exchange coefficients were calibrated, a conservative constituent, chloride, was simulated using the LM2 model configuration to verify that the water transport components described above were a good representation of the overall water transport field for the LM2-Toxic. The chloride model was run just once without adjusting any parameter or coefficient. The model results had very good agreement with the observations during the LMMBP period (Appendix 4.5.4). A detailed discussion of the chloride results can be found in Part 4, Chapters 4 and 5.

4.3.4 Solid Balance

PCBs have an affinity for organic carbon. Each type of organic carbon sorbs PCBs differently. Settling rates and resuspension rates, decay rates, etc., impact the organic carbon fractions. Figure 4.3.4 shows the conceptual framework and the processes related to organic carbon sorbent dynamics in Lake Michigan. Three organic carbon sorbents were simulated as state variables in LM2-Toxic. They were biotic carbon (BIC), particulate detrital carbon (PDC), and dissolved organic carbon (DOC). BIC
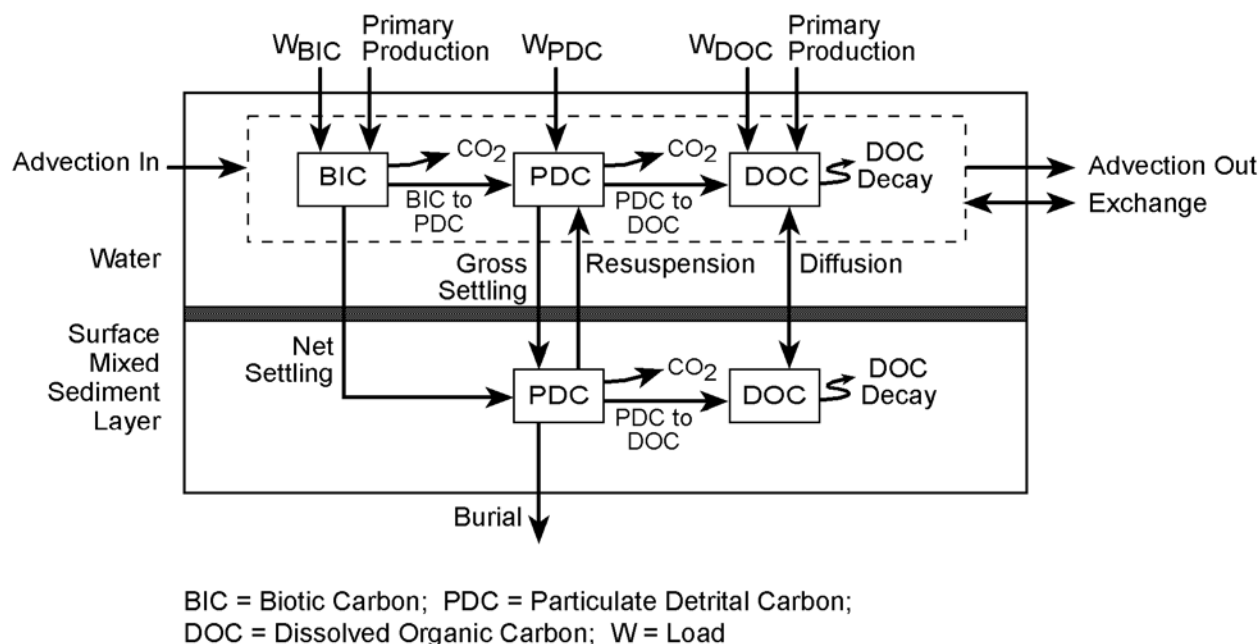
BIC = Biotic Carbon; PDC = Particulate Detrital Carbon;
DOC = Dissolved Organic Carbon; W = Load

Figure 4.3.4. Conceptual framework of organic carbon sorbent dynamics used in the LM2-Toxic model.

represented particulate organic carbon (POC) in live phytoplankton biomass. PDC represented particulate detrital carbon derived from phytoplankton decomposition, zooplankton excretion, and allochthonous sources. DOC represented colloidal-sized particles that pass through ashed 47 mm diameter glass fibers (U.S. Environmental Protection Agency, 1997).

Other than the components related to the water transport field, numerous processes were considered important in controlling the three organic carbon solids concentrations in either the water column or sediment or both (Table 4.3.3).

The segment-specific internal primary production load generated from the eutrophication model (LM3-Eutro) was a crucial input to the LM2-Toxic. Primary production is the dominant organic carbon load to Lake Michigan. LM3-Eutro generated primary production accounted for over 90 percent of the total POC load to the lake. Further discussions on parameterization of processes such as organic carbon sorbent decay and resuspension are presented in the following sections. In Chapter 4, detailed discussion of the input data used in the processes related to organic carbon dynamics will be provided.

4.3.4.1 Solid Kinetics

Decay of organic carbon sorbent was the only kinetic process considered for solid dynamics in the LM2-Toxic. This process transforms significant amounts of carbon species in both the water column and sediment segments. To capture general carbon sorbent loss mechanisms in the water column without introducing too much complication, pseudo-first-order carbon decay rates for BIC, PDC, and DOC were formulated as Michaelis-Menten functions of respective carbon concentrations and then temperature-corrected according to an Arrhenius relationship with a temperature coefficient, $\theta = 1.05$ (Bierman *et al.*, 1992). The decay equations for the three organic carbon sorbents in water column are:

$$k_{d(BIC)} = \left(\frac{\hat{k}_{d(BIC)} * C_{BIC}}{k_{1/2(BIC)} + C_{BIC}} \right) * \theta^{(T-20)} \qquad (4.3.3)$$

$$k_{d(PDC)} = \left(\frac{\hat{k}_{d(PDC)} * C_{PDC}}{k_{1/2(PDC)} + C_{PDC}} \right) * \theta^{(T-20)} \qquad (4.3.4)$$

232

Table 4.3.3. Processes Considered in Organic Carbon Sorbent Dynamics Constructed for the LM2-Toxic

Biotic Carbon (BIC)	Particulate Detrital Carbon (PDC)	Dissolved Organic Carbon (DOC)
External Tributary Loads	External Tributary Loads	External Tributary Loads
Internal Primary Production Loads	Yield From BIC Decay	Internal Loads Derived From Primary Production Loads
Net Settling	Gross Settling	Yield From PDC Decay
Decay and Yield to PDC	Resuspension	Diffusion at Sediment-Water Interface
	Decay and Yield to DOC in Both Water Column and Sediments	Decay in Both Water Column and Sediments
	Burial to Deeper Subsurface Sediment Layer	

$$k_{d(DOC)} = \left(\frac{\hat{k}_{d(DOC)} * C_{DOC}}{k_{1/2(DOC)} + C_{DOC}} \right) * \theta^{(T-20)} \qquad (4.3.5)$$

where

k_d = decay rate of a carbon sorbent in water column (d^{-1})

$\hat{k}_d$ = substrate saturated decay rate of a carbon sorbent in water column at 20°C (d^{-1})

$k_{1/2}$ = Michaelis-Menten half-saturation constant for a carbon sorbent in water column (mg C/L); where C = carbon, L = liter

C = segment-specific concentration of a carbon sorbent in water column (mg C/L); where C = carbon, L = liter

θ = Arrhenius temperature coefficient (dimensionless)

T = measured segment-specific temperature (°C)

Therefore, the final decay rates for the carbon sorbents were temperature- and spatially-dependent.

The rates were calculated at each time step during the model simulation period. Simpler equations were used for decay of carbon species in the surficial segments. BIC in sediments was assumed to be zero. The equations used for PDC and DOC decay in sediments were:

$$k_{ds(DOC)} = \bar{k}_{ds(DOC)} * \theta^{(T-20)}$$

$$k_{ds(PDC)} = \bar{k}_{ds(PDC)} * \theta^{(T-20)} \qquad (4.3.6)$$

where

k_{ds} = segment-specific and temperature-dependent decay rate of a carbon sorbent in sediments (d^{-1})

$\bar{k}_{ds}$ = decay rate of a carbon sorbent in sediment at 20°C

T = measured segment-specific temperature (°C)

4.3.4.2 Sediment Transport

The transport and fate of PCBs in natural waters and sediments are governed by the transport and fate of POC. Based on the data collected during the

LMMBP period, sediment PCB concentrations were approximately four or five orders of magnitude higher than water column PCB concentrations. The interaction between the water column and surficial sediments for POC was critical to PCB dynamics, mass budget, and especially long-term concentration in the lake. Therefore, it was necessary to describe the important processes involved in vertical particle transport, including settling velocity, resuspension rate, and burial rate within the LM2-Toxic. There is no unique set of carbon solids transport rates that could be determined without the aid of a solids tracer compound (Thomann and Di Toro, 1983; DePinto, 1994). Even though the burial rate could be fixed based on the Pb-210 core dating technique, there still was an infinite set of settling and resuspension rates that could close the solids mass balance for vertical particle transport.

4.3.4.2.1 Steady-State Resuspension Calibration

The overall modeling design for the LM2-Toxic was intended to minimize the parameters needing to be calibrated. It was originally planned not to calibrate any particle transport parameters, including the sediment resuspension rate. The original plan was that LM3-Eutro and SEDZL would provide carbon sorbent settling velocities and estimate POC resuspension rates, respectively. However, it was not clear in late 1999 that the particle transport rates would be available in time for the LM2-Toxic execution due to the departures of key project personnel. After a series of discussion among staff, it was decided that a steady-state PDC mass balance approach would be used. A similar approach was used for the Green Bay Mass Balance Project (GBMBP) (Bierman *et al.*, 1992). This approach was used to estimate the segment-specific sediment POC resuspension. In the water column, POC = BIC + PDC, while in the sediment, POC = PDC.

There was only one sediment layer specified in LM2-Toxic model segmentation (Figure 4.3.3). The thickness of each surficial mixing sediment segment was estimated based on the surficial sediment mixing layer thickness derived from the LMMBP box cores (Robbins *et al.*, 1999). Figure 4.3.5 shows a schematic of the concepts used for the steady-state PDC mass balance analysis. Due to the simple sediment segmentation within the LM2-Toxic, the procedure for determining the segment-specific
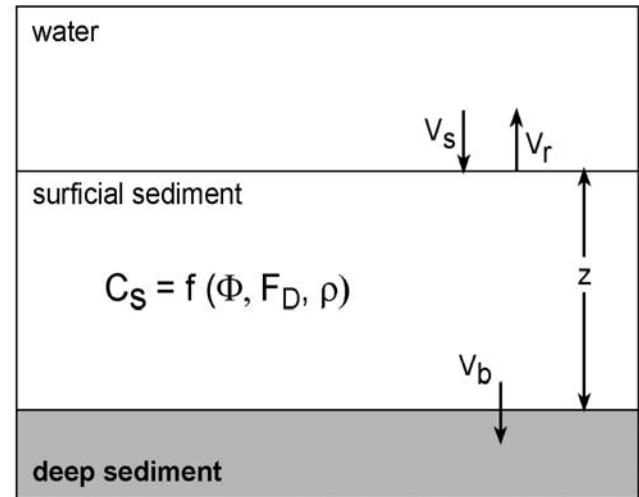

Figure 4.3.5. Schematic of conceptualization for the steady-state mass balance analysis for PDC vertical transport where ϕ = porosity (dimensionless), F_D = fraction of organic carbon, g_{dw}/g, ρ = bulk density of surficial sediments, wet weight, g/cm^3.

sediment PDC resuspension velocities was much more simplified. The set of PDC mass balance equations for each sediment segment for PDC vertical transport was reduced to only one. The simplified equation can be written as:

$$V_s \frac{dC_s}{dt} = v_s * A * C_w - v_r * A * C_s$$
$$- v_b * A * C_s - k_{ds} * V_s * C_s$$

(4.3.7)

At steady-state, $\frac{dC_s}{dt}$ = 0, and V_s = A*z, the resuspension velocity can be solved as:

$$v_r = \frac{v_s * C_w - v_b * C_s - k_{ds} * z * C_s}{C_s}$$

(4.3.8)

where

V_s = volume of the surficial sediment segment (m^3)

C_s = bulk concentration of PDC in the surficial sediment segment (mg C/m^3); where C = carbon

v_s = PDC gross settling velocity (m/d)

234

A = PDC settling area for a surficial sediment segment (m^2)

C_w = effective PDC concentration in water column segment right above the sediment segment (mg C/m^3); where C = carbon. $C_w = C_{wPDC} + (v_{sBIC}/v_{sPDC})*C_{wBIC}$, where v_{sBIC} = BIC gross settling velocity, m/d; $v_{sPDC} = v_s$ = PDC gross settling velocity, m/d; C_{wPDC} = PDC concentration in the water column segment, mg C/m^3; C_{wBIC} = BIC concentration in the water column segment, mg C/m^3.

v_r = PDC resuspension velocity (m/d)

v_b = sediment (PDC) burial rate (m/d)

k_{ds} = PDC decay rate in sediments (d^{-1})

z = thickness of the surficial sediment mixing layer (m)

Equation 4.3.8 was manipulated differently for different sediment zones. In the areas where the water depth was greater than 100 m, resuspension was considered as non-wave-induced resuspension. The resuspension rates in these areas were directly calculated using Equation 4.3.8. Although it is arguable that there is any resuspension in the area above which the water is deeper than 100 m (Part 1, Chapter 4), the resuspension rate used in LM2-Toxic was estimated. This was because of a lack of available sediment transport models that were well tested for not only accurately computing sediment resuspension rate, but also satisfying the particle mass balance in both water column and sediments under this kind of coarse spatial resolution used in LM2-Toxic. After combining wave height information for Lake Michigan estimated for the LMMBP period, resuspension velocities in non-depositional areas were computed using empirical wave-induced resuspension derived from Equation 4.3.8. Further detailed data reductions and discussion of the parameters used in Equation 4.3.8 will be provided in Chapters 4 and 5.

4.3.4.2.2 Empirical Wave-Induced Resuspension Calculation

An equation similar to the one used in the GBMBP (Bierman *et al.*, 1992) was developed for LM2-Toxic

to estimate the resuspension rates in non-depositional zones. The equation is:

$$v_r = \alpha(W - W_{cr}) \qquad (4.3.9)$$

where

v_r = estimated daily, segment-specific resuspension velocity (m/d)

W = segment-specific surface daily average wave height (m)

W_{cr} = segment-specific critical wave height for the segment below which there is no wave-induced resuspension (m)

α = segment-specific empirical wave coefficient (d^{-1})

Due to lack of accurate ice cover information and winter concentrations of BIC and PDC during the LMMBP period, it was not feasible to estimate the segment-specific base ($W < W_{cr}$) resuspension velocity (v_{r0}, i.e., non-wave-induced resuspension in non-depositional area) formulated in the original wind-induced resuspension calculation presented in the GBMBP report (Bierman *et al.*, 1992). Therefore, v_{r0} was removed from the original formula used in the GBMBP report (Bierman *et al.*, 1992). This made the resuspension in the non-depositional areas a function of wave heights, as shown in Equation 4.3.9.

As part of the LMMBP, Schwab and Beletsky, using the NOAA/Great Lakes Environmental Research Laboratory (GLERL) Donelan wave model, generated surface wave heights (Schwab and Beletsky, 1998). These values were made available on a high-resolution grid of 5 x 5 km^2 and on time scales of one-hour. These data were then averaged and aggregated on a daily basis for the 53 sediment segments used in LM2-Toxic. The segment-specific empirical wave coefficient (α) was estimated using the following equation:

$$\bar{v}_r = \alpha\left[\frac{1}{n}\sum_{j}^{n}(W_j - W_{cr})\right] \qquad (4.3.10)$$

where

$\overline{v}_r$ = segment-specific average resuspension velocity calculated for Equation 4.3.8 (m/d)

n = number of days during LMMBP period

W_j = segment-specific daily wave height (m)

Note: The term (W_j - W_{cr}) in the Equation 4.3.10 becomes zero when $W_j < W_{cr}$.

The Equation 4.3.10 was derived under the assumption that the cumulative resuspension flux computed from Equation 4.3.9 on a daily basis for the LMMBP period was equal to the total resuspension flux computed for the same period from the steady-state sediment carbon mass balance in Equation 4.3.8. The empirical wave coefficient (α) was then formulated as:

$$\alpha = \frac{\overline{v}_r}{\frac{1}{n} \sum_{j}^{n} (W_j - W_{cr})}$$
  4.3.11

The segment-specific critical wave height (W_{cr}) was a very crucial parameter for calculating wave-induced resuspension flux. The availability of field data relating local resuspension to surface critical wave heights was extremely important for defining the segment-specific or depth-specific critical wave heights in this approach. Fortunately, a relatively good set of the wave-induced resuspension field data (Appendix 4.3.1) was available to use with a great deal of help from Nathan Hawley at NOAA/GLERL (Hawley, 1999). The data set included the critical wave heights required for resuspension and the water depths at which local sediment resuspension was observed. These data were based on 30 deployments during 1994-2000 for which sediment concentration near the bed were plotted against the wave heights from the GLERL/Donelan wave model (Schwab and Beletsky, 1998). Figure 4.3.6 shows deployment locations in Lake Michigan during this period (Lesht and Hawley, 1987; Hawley, 1999; Hawley, 2001). The details on this method are discussed in Lesht and Hawley (1987) and Hawley (1999, 2001). The deployment locations were limited to the southwest region of the lake and the number of the deployments were relatively small. There were
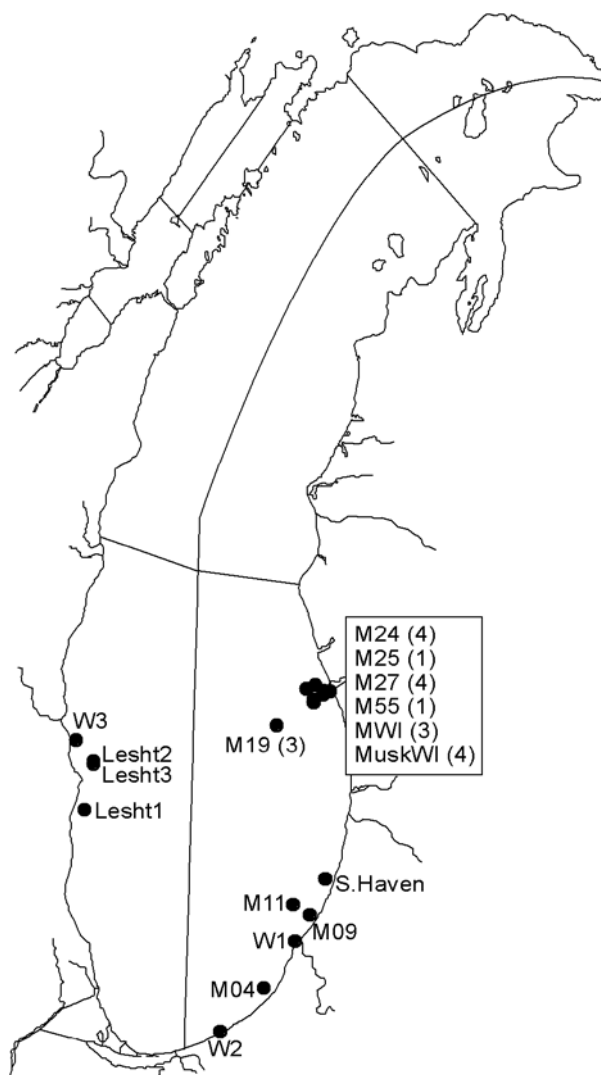

Figure 4.3.6. Locations of the 30 deployments between 1994 and 2000.

indications that for similar water depths, different surface critical wave heights were required to resuspend sediment in different regions of the lake (Hawley, 2001). However, the data set was the best available data (Appendix 4.3.1) and was applied to the sediment segments within the depositional area.

Based on this data set, a simple linear regression was performed on the data (deployment depth, critical wave height) for stations at which local resuspension occurred (Figure 4.3.7). Visual examination of Figure 4.3.7 revealed that the linear regression line was a reasonable approximation of

236

Relation b/w Critical Wave Height and Station Depth
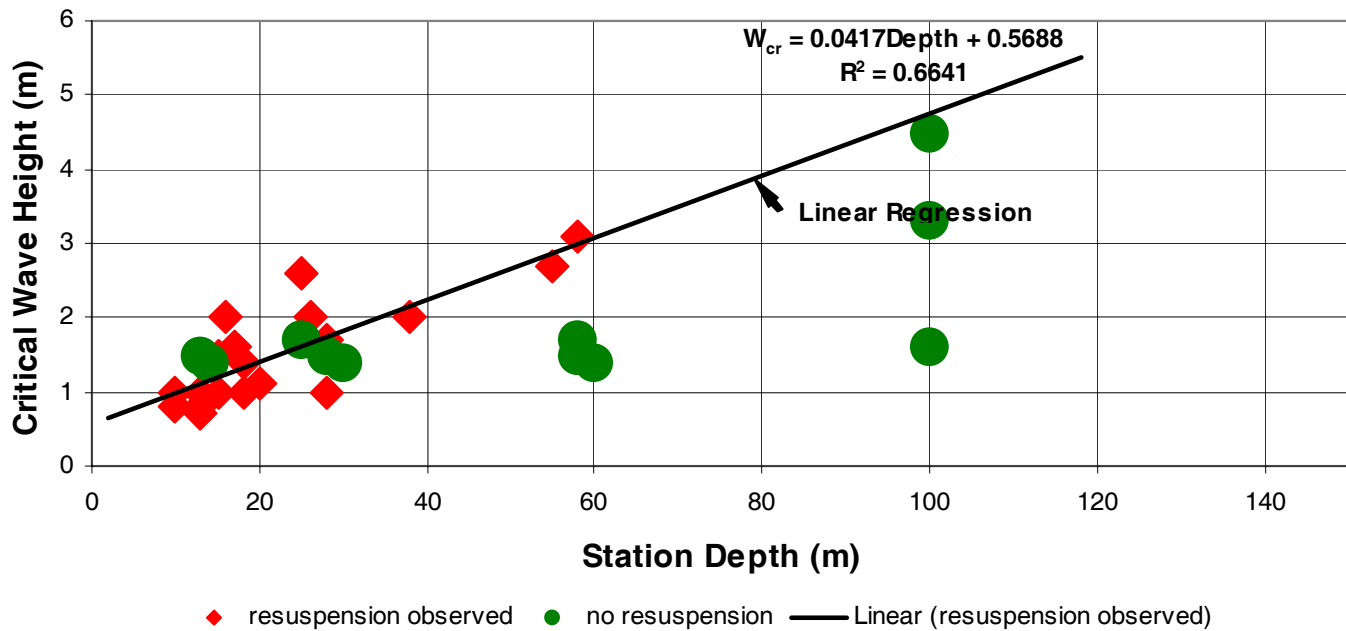### (Data provided by Nathan Hawley, NOAA, GLERL)

Figure 4.3.7. Regression analysis on the data set (resuspension observed only). For the convenience of the viewer, the data at the stations with no resuspension observed are also put on this plot.

the relationship between water depth and critical wave heights.

Assuming this linear relationship between the critical wave height and water depth, the parameterization of the segment-specific critical wave height (W_{cr}) is:

$$W_{cr} = 0.0417 * Depth + 0.5688 \qquad (4.3.12)$$

where

$Depth$ = deployment depth at the resuspension station (m)

Therefore, the daily wave-induced resuspension in the non-depositional area was calculated using Equation 4.3.9 given the segment-specific parameters α and W_{cr}.

For the 30 deployments used to calculate the relationship, there were 11 cases with no resuspension observed. These deployments were either at very large depths or occurred during the

stratified period. Previous observations (Lesht and Hawley, 1987; Hawley, 1999; Hawley and Lesht, 1995; Hawley and Murthy, 1995), combined with those listed in Appendix 4.3.1, lead to the conclusion that resuspension events during the stratified period are confined to shallow water regions (< 13 m) where the epilimnion was the entire water column. It is arguable whether Equation 4.3.12 should be applied to both unstratified and stratified periods. Based on Nathan Hawley's suggestion (Hawley, 2001) and data in Appendix 4.3.1, separate criteria for unstratified and stratified periods were unnecessary. Therefore, it was decided that the Equation 4.3.12 would be used in the wave-induced resuspension calculation without considering seasonal variability.

4.3.4.2.3 The Sediment Bed – Semi-Lagrangian Option

Another important aspect related to sediment transport was constructing the sediment bed. The Semi-Lagrangian sediment bed option in IPX Version 2.74 (Velleux *et al.*, 2000) was incorporated into the

LM2-Toxic model by taking advantage of the flexibility in IPX, which allows a moving sediment-water interface. Unlike the Eulerian option, the Semi-Lagrangian option does not allow material to move into or out of the modeled system across the sediment bottom boundary. Therefore, the system being modeled would not be artificially introducing or losing mass through the sediment bed, especially for cases when the total inventory of sediments is not well-defined. In this option, the solids concentration in all sediment segments was held constant. The volume (thickness) of all surficial sediment segments was allowed to vary from their initial values in response to net settling and net resuspension fluxes. In response to net settling (deposition), the thickness of the surficial sediment segment increased, and the segment was split into two vertically adjacent segments when its maximum thickness was reached. In response to net resuspension (scouring), the thickness of the surficial sediment segment decreased, and the subsurface sediment segment replaced the surficial sediment segment when its minimum thickness was reached. When there was not enough sediment to be resuspended, the resuspension was stopped regardless of the resuspension velocity specified. Once sediment was deposited, the resuspension was resumed in the surficial sediment segment.

4.3.5 Chemical Balance

The transport and fate of hydrophobic organic chemicals such as PCBs are closely linked to the movement of carbon sorbents. The approaches used in the past to model PCBs for the Great Lakes were based on either homolog or total PCBs. LM2-Toxic is a PCB congener-based model. It simulates 54 PCB congeners that accounted for roughly 70% of the total PCB mass in Lake Michigan. Figure 4.3.8 shows the conceptual framework and processes related to PCB dynamics in Lake Michigan. Four phases were simulated in the LM2-Toxic for the congeners. The four phases were dissolved, sorbed to PDC, sorbed to BIC, and bound to DOC. The processes considered important for PCB dynamics in Lake Michigan water column and sediments are:
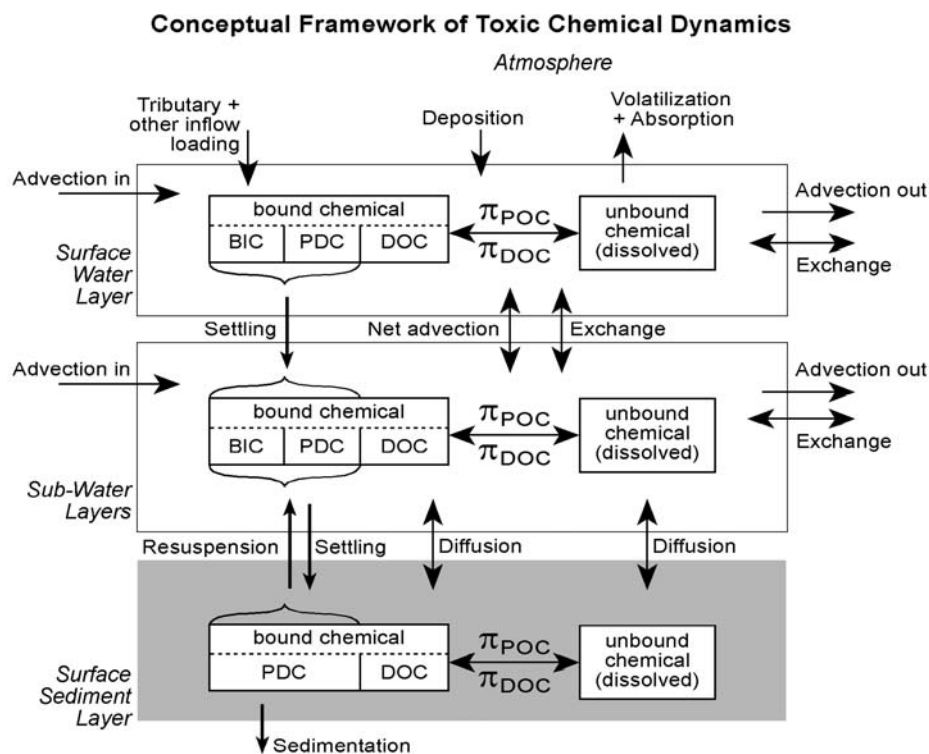

Figure 4.3.8. Conceptual framework used by the LM2-Toxic model for PCB congeners in Lake Michigan.

- Equilibrium partitioning between dissolved phase and sorbed phases of PCBs.

- Air-water exchange of dissolved PCBs including both volatilization and absorption.

- External loadings of PCBs including tributary loads and atmospheric wet and dry deposition.

- Gross settling of particulate PCBs.

- Resuspension of particulate PCBs.

- Pore-water diffusion of dissolved PCBs at the sediment-water interface.

- Advection across interfaces between water segments.

- Dispersion of PCBs across interfaces between water segments.

- Sediment burial of PCBs.

The following subsections present detailed descriptions of PCB equilibrium partitioning, PCB air-water exchange, and parameters associated with these processes.

4.3.5.1 PCB Partitioning

Due to PCBs' hydrophobic nature, the partitioning process and the movement of organic carbon particles were very important for describing the transport and fate of PCBs in Lake Michigan. Therefore, estimation of PCB partitioning coefficients was one of the major steps to secure a successful calibration of LM2-Toxic.

Partitioning of a hydrophobic organic contaminant such as PCBs in a dilute water system is, in general, governed by the following relationship (Eadie *et al.*, 1990, 1992; Bierman *et al.*, 1992):

$$K_p = \frac{C_p}{mC_d} \qquad (4.3.13)$$

where

K_p = partitioning coefficient (L/kg)

C_p = particle associated contaminant (PCBs) concentration (kg/L)

m = sorbent (either total suspended solid, total suspended matter (TSM), or POC in LM2-Toxic concentration (kg/L)

C_d = dissolved PCBs concentration (kg/L)

Based on this fundamental equation, two of the many partition theories have been widely used to describe the distribution of PCBs in a diluted water system such as a lake or a river. These were a two-phase PCB partitioning model and a three-phase PCB partitioning model (Swackhamer and Armstrong, 1987; Eadie *et al.*, 1990, 1992; Bierman *et al.*, 1992).

In the two-phase PCB partitioning model, PCBs is either in dissolved phases or in a particulate phase. The dissolved phases include both dissolved PCBs and PCBs sorbed to DOC. The particulate phase is the PCBs sorbed to POC (POC = BIC + PDC). The partition coefficient is described as:

$$K'_{POC,\alpha} = \frac{C_{POC}}{[POC]\,C_{d,\alpha}} \qquad (4.3.14)$$

where

$K'_{POC,\alpha}$ = *in situ* partition coefficient for PCBs on POC (L/kg OC)

C_{POC} = concentration of PCBs bound to POC (kg/L)

$[POC]$ = concentration of POC (kg OC/L)

$C_{d,\alpha}$ = concentration of PCBs in an analytically defined dissolved phase (i.e., dissolved and sorbed to DOC) (kg/L)

The two-phase model is a very simple, straight-forward method and most commonly used to quickly compute the *in situ* POC partition coefficients ($K'_{POC,\alpha}$) for PCB congeners without using sophisticated statistical analysis. The computed $K'_{POC,\alpha}$ can then be conveniently compared to the measured octanol-water partition coefficient K_{OW} (Karickhoff, 1981; Baker and Eisenreich, 1986; Swackhamer and Armstrong, 1987; Bierman *et al.*, 1992).

In the three-phase PCB partitioning model, PCBs was distributed between the dissolved, POC particulate, and DOC particulate phases. The partition coefficients are defined as follows:

$$K_{DOC} = \frac{C_{DOC}}{[DOC]\,C_d} \qquad (4.3.15)$$

and

$$K'_{POC} = \frac{C_{POC}}{[POC]\,C_d} \qquad (4.3.16)$$

where

K_{DOC} = partition coefficient for PCBs on DOC (L/kg OC)

K'_{POC} = *in situ* partition coefficient for PCBs on POC (L/kg OC)

$[DOC]$ = DOC concentration (kg OC/L)

C_{DOC} = concentration of PCBs bound to DOC (kg/L)

C_d = dissolved PCB concentrations (kg/L)

The total concentration of PCBs (C_T) equals the sum of the three phases:

$$C_T = C_d + C_{DOC} + C_{POC}$$

$$= C_d (1 + K_{DOC}[DOC] + K'_{POC}[POC])$$
$$(4.3.17)$$

Because of the difficulty of directly measuring dissolved PCB concentrations (C_d), the POC (K'_{POC}) partition coefficients had to be estimated using either a simple linear regression technique (Brannon *et al.*, 1991; Bierman *et al.*, 1992) or a statistical analysis such as a combination of the Levenberg-Marquardt nonlinear least squares routine and root mean square error algorithm (Bierman *et al.*, 1992). The initial estimation of the K'_{POC} and K_{DOC} for each selected PCB congener (total 40 congeners) was done by applying the simple linear regression technique to the following equation for the LMMBP-generated data (see Karickhoff *et al.*, 1979 and

Bierman *et al.*, 1992 for detailed derivation of this equation).

$$\frac{C_{d,\alpha}[POC]}{C_{POC}} = \frac{K_{DOC}}{K'_{POC}}[DOC] + \frac{1}{K'_{POC}} \qquad (4.3.18)$$

The terms on the left-hand side and [DOC] on the right-hand side are the measured concentrations for each water column sample. The simple linear regression was applied to the above equation to yield a slope of K_{DOC}/K'_{POC} and an intercept of $1/K'_{POC}$. From this, both partition coefficients K'_{POC} and K_{DOC} were calculated. Pairs of partition coefficients were estimated by repeating the regression analysis for each PCB congener selected.

After a thorough analysis of the PCB congener partitioning coefficient results estimated using both the two- and three-phase partitioning models, the two-phase partitioning model was selected as the approach to initially compute the POC partition coefficients ($K'_{POC,\alpha}$) that would be used in LM2-Toxic. It was selected because 1) the two-phase partitioning model was simple and very efficient in terms of data analysis procedure; 2) though the regression technique used in the three-phase partitioning model worked well for a well-behaved system, it was not applicable to a natural water system with heterogeneous organic carbon concentrations, PCB characteristics, and PCB concentrations; and 3) the three-phase model-estimated PCB congener partitioning coefficients on DOC (K_{DOC}) did not have similar trends as the ones on POC (K'_{POC}). Previous publications suggested that the K_{DOC} and K'_{POC} of PCB congeners should have similar variation trends, and that the value of K_{DOC} should be within 1 to 2 orders of magnitude less than the value of K'_{POC} (Carter and Suffet, 1982; Landrum *et al.*, 1984, 1987; Hassett and Milicic, 1985; Chiou *et al.*, 1986, 1987; Eadie *et al.*, 1990, 1992; Bierman *et al.*, 1992).

4.3.5.2 PCB Air-Water Exchange

Previous studies (Endicott *et al.*, 2005; Endicott, 2005; DePinto *et al.*, 2003) have suggested that net volatilization to the atmosphere may be the predominant loss mechanism for hydrophobic organic contaminants such as PCBs in Great Lakes. Therefore, it was very important to precisely compute

the net PCB mass transfer across the water-air interface in order to satisfy the overall PCBs inventory and mass budget in the Lake Michigan system for the LMMBP period, and forecast PCB concentrations in both the water column and sediments with a certain degree of confidence. The mass change rate term ($S_{\alpha w,j}$) for PCBs due to air-water exchange processes in Equation 4.3.19 was calculated as a product of the overall net mass exchange flux and surface area of the water segment j.

$$S_{\alpha w,j} = \left[k_{ol} * (C_{dw,j} - \frac{C_{\alpha,j}}{H'}) \right] * A_j \qquad (4.3.19)$$

where

k_{ol} = the overall mass exchange rate coefficient (m/d)

C_{dw} = dissolved PCB concentrations in water (ng/m^3)

C_{α} = atmospheric PCB concentrations (ng/m^3)

H' = temperature dependent Henry's Law Constant for a PCB congener (dimensionless)

A_j = surface area of the water segment j (m^2)

The overall mass exchange rate coefficient (k_{ol}) was calculated using the Whitman two-film theory formulation (Whitman, 1923) given as:

$$k_{ol} = \frac{1}{\frac{1}{k_l} + \frac{1}{K_g * H'}} \qquad (4.3.20)$$

where

k_l = the liquid film mass transfer rate coefficient (m/d)

k_g = the gas film mass transfer rate coefficient (m/d)

The LMMBP Atmospheric Workgroup recommended that the Wanninkhoff (Wanninkhoff, 1992) formulation for water mass transfer resistance and the

Schwarzenbach (Schwarzenbach *et al.*, 1993) formulation for gas mass transfer resistance were the most appropriate for modeling the air-water exchange of PCBs in Lake Michigan. The Wanninkhoff equation for k_l, with correction for PCBs molecular diffusivity in reference to carbon dioxide (CO_2) molecular diffusivity across the air-water interface, is given as:

$$k_l = 0.45 * \left(\frac{D_w}{D_{l\_CO_2}} \right)^{\frac{1}{2}} * u_{10}^{1.64} \qquad (4.3.21)$$

where

D_w = chemical molecular diffusivity in water (cm^2/s)

$D_{l\_CO_2}$ = CO_2 molecular diffusivity in water (cm^2/s)

u_{10} = wind velocity measured at 10 m above water surface (m/s)

The Schwarzenbach formulation for k_g with correction of PCB molecular diffusivity in reference to water vapor molecular diffusivity across the air-water interface is given as:

$$k_g = (0.2 * u_{10} + 0.3) * \left(\frac{D_\alpha}{D_{g\_H_2O}} \right)^{0.61} \qquad (4.3.22)$$

where

D_α = chemical molecular diffusivity in air (cm^2/m)

$D_{g\_H_2O}$ = water vapor molecular diffusivity in gas phase (cm^2/m)

Another recommendation from the LMMBP Atmospheric Workgroup was to use the equation of Henry's Law Constant for PCB congeners updated by Bamford using recently developed data (Bamford *et al.*, 2000). The equation originated from the Gibbs-Helmholtz equation as:

$$lnH' = -\frac{\Delta H_H}{R * T} + \frac{\Delta S_H}{R} \qquad (4.3.23)$$

Afer rearranging the equation, the temperature dependent Henry's Law constant is given as:

$$H' = e^{\left(-\frac{\Delta H_H}{R * T} + \frac{\Delta S_H}{R}\right)} \qquad (4.3.24)$$

where

H' = temperature dependent Henry's Law Constant (dimensionless)

ΔH_H = the enthalpy of phase change for a PCB congener (kJ/mol)

ΔS_H = the entropy of phase change for a PCB congener (kJ/mol)

R = the ideal gas constant, 8.315×10^{-3} kJ/(mol)(°K)

T = interfacial temperature (°K)

These volatilization formulas were coded into subroutines of LM2-Toxic, and the parameters H', k_l, and k_g were calculated at every time step for each LM2-Toxic segment.

4.3.5.3 PCB-Specific Parameterization

PCB congener-specific parameters input into LM2-Toxic model included PCB congener partitioning coefficients, molecular weight, enthalpy, and entropy. Chapter 4 of this part provides detailed information on the values used in the LM2-Toxic for these parameters, their data sources, and parameterization procedures.

4.3.6 Modification

LM2-Toxic features some important updates from both the IPX and GBTOX models. The project-specific modifications were:

- Incorporation of organic carbon sorbent dynamics used in GBMBP (Bierman *et al.*, 1992).

- Organic carbon kinetic processes and biotransformation.

- Incorporation of the quasi-Lagrangian framework for sediment transport scheme used in the IPX model.

- Added the Gibbs-Helmholtz formulation (Bamford *et al.*, 2000) to compute the Henry's Law Constant for PCB congeners.

- Added the Wanninkhoff formulation for liquid film mass transfer rate coefficient and the Schwarzenbach formulation for gas film transfer rate coefficient in the PCB overall volatilization equations.

- Para meterization of segment-specific resuspension velocity of carbon sorbent (PDC) as a function of daily average wave height.

- Added subroutines for performing segment-specific and lake-wide mass budget calculations, a very useful tool to identify programming errors, to identify artificial gain/loss of solid/chemical mass to a water system, and to construct overall mass budget for the system simulated.

- Capability for specifying segment-specific and daily water temperature time functions.

- Capability for specifying segment-specific and daily air temperature time functions.

- Capability for specifying segment-specific and daily wind speed time functions.

- Capability for specifying segment-specific, PCB congener-specific, and daily atmospheric PCB concentration time functions.

- Reorganization/rewrite of many subroutines and minor bug fixes to Euler integration. Use of utility libraries and organized error handling (UT library) in the codes. Modification to input format - using FIREAD.

LM2-Toxic was developed and tested on both the Unix and the Linux platforms and used both FORTRAN 77 and FORTRAN 90 compilers.

242

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